Hydrogen Cyanide and Smoke Particle Characteristics During Combustion of Polyurethane Foams and Other Nitrogen-Containing Materials

Development of a Test Parameter

By Maria I. De Rosa and Charles D. Litton

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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Manuel Lujan, Jr., Secretary

BUREAU OF MINES
T S Ary, Director

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	μg/g	microgram per gram
°C/min	degree Celsius per minute	min	minute
cm	centimeter	mL	milliliter
cm^2/p	square centimeter per particle	pct	percent
g	gram	p/cm^2	particle per square centimeter
L	liter	p/cm^3	particle per cubic centimeter
L/min	liter per minute	ppm/g	part per million per gram
mg/g	milligram per gram	p/($cm^2 \cdot$ g)	particle per square centimeter per gram
μm	micrometer	s	second

HYDROGEN CYANIDE AND SMOKE PARTICLE CHARACTERISTICS DURING COMBUSTION OF POLYURETHANE FOAMS AND OTHER NITROGEN-CONTAINING MATERIALS

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By Maria I. De Rosa[1] and Charles D. Litton[2]

ABSTRACT

The U.S. Bureau of Mines performed experiments to determine the hydrogen cyanide (HCN) concentrations and smoke particle characteristics during the combustion of flexible polyurethane foams and other nitrogen-containing materials, for the development of a test parameter. The experiments were conducted in an approximately 20-L furnace at set furnace temperatures of 250° and 1,000° C for a 14-min duration, with an airflow through the furnace of 10 L/min. The variables studied as a function of time were the gaseous and aerosol HCN concentrations, the smoke particles average diameter (d_g) and particle concentration (n_o), and the product of the smoke particle diameter and concentration ($d_g n_o$). Carbon monoxide, carbon dioxide, and oxygen concentrations, sample mass weight loss, and furnace temperatures were also studied; analyses of nitrogen and cyanate content of the material were carried out. Results show that $d_g n_o$ correlates directly with the HCN concentrations, which depend on the nitrogen and cyanate contents of the material.

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INTRODUCTION

In 1984, the U.S. Bureau of Mines, within its mission to create and maintain safety in the mines and, specifically, to assess the hazard of mine materials during fire, initiated a series of experiments to characterize smoke particles and primary gas toxicities evolved during the combustion of mine materials, for the development of test parameters. It was found $(1-7)$[3] that $d_g n_o$ correlated with the primary gas toxicity (hydrogen chloride, HCl) evolved in large quantities even during the early ($\sim300°$ C) combustion of polyvinyl chloride and chlorinated mine materials. The higher the HCl concentrations, the higher the inverse of the product $d_g n_o$, $1/d_g n_o$. It may be reasoned that at a low value of $d_g n_o$ (or at a higher value of its inverse, $1/d_g n_o$) a

large percentage of the consumed mass is available for HCl production rather than smoke. In this study, the Bureau set out to determine the HCN (gaseous and aerosol) concentrations, the mass particulates on which the cyanide aerosol embed itself, and smoke particles, with given characteristics such as d_g, n_o, and $d_g n_o$, evolved during the combustion of nitrogen-containing materials such as treated and untreated flexible polyurethane foams, nylon and wool fabrics, and, for comparison purpose, treated cotton batting. Correlations among the variables may lead to the development of simple and inexpensive test parameters to assess the toxic hazard of these materials during fire.

BACKGROUND

The thermal degradation of plastics involves the emission of many volatile substances, which may create serious life hazard under fire conditions. The qualitative and quantitative composition of the substances evolved depend on the type of material, the thermal degradation temperature, and the oxygen concentration (8). At temperatures up to 400° C, plastics decompose forming complex products; within the temperature range of 400°- 700° C, often the highest concentrations of a variety of substances are observed (9). Widely used and hazard creating plastics are flexible polyurethane foams, which are manufactured commercially by mixing an isocyanate (tolylene 2.4-disocyanate) with a polyol containing a hydroxyl group (ethylene glycol); amines are added to the volatile liquid mixture to produce a felting compound comparable to that of microfibers.

The major drawback of these foams, however, is that they can easily ignite, burning at fast rates. The reason may be that the nitrogen content of polyurethanes is much lower than that of other natural nitrogen-containing polymers such as wool, which has been found to ignite at higher temperatures, burning at lower rates. At relatively low temperatures (200°-300° C), a polyurethane bond cleavage takes place with the evolution of HCN with a short-term exposure limit (STEL) of 15 ppm; and immediately dangerous to life and health (IDLH) at a concentration of 50 ppm; isocyanates react spontaneously with compounds containing active hydrogen atoms, which migrate to the nitrogen (10). Chemical analyses have shown that HCN is generated from one or more

nitrogen-containing compounds in the foam (11). Furthermore, at higher temperatures ($>400°$ C), multiple nitrogen-containing compounds contribute to additional cyanide structure in the char; in fact, the nitrogen-containing compounds in the char are more likely to generate HCN when heated than the nitrogen-containing molecules in the original foam (12). Carbon monoxide (CO; STEL, 400 ppm; IDLH, 1,500 ppm) also evolves in large quantities at higher temperatures, although HCN concentrations have higher toxicity (13). CO and HCN toxicities have been found to be additive (14). Furthermore, other toxic substances evolve such as acrylonitrile, benzonitrile, benzene, toluene, and pyridine.

The cyanide ion of cyanide compounds, rapidly absorbed in the blood, inhibits the enzymes required for the respiration of cells, preventing the uptaking of oxygen by the tissues and causing motor weakness of arms and legs, severe irritation of the nose, and finally death by asphyxia; at very low dosages, symptoms of HCN exposure may be weakness, headaches, confusion, nausea, and vomiting (15).

The ignitability of flexible polyurethane foam can be decreased by the use of additives and reactive flame retardants, which include halogens and/or phosphorus containing polyols. The phosphorus during the early stage of combustion produces a thick, charry crust that protects the underlying 80-85 pct of the polymer.

Nylons, aliphatic polyamides, containing the recurring amide group-CONH—, may be formed by either polycondensation of a diamine and a dibasic acid (nylon 6,6), or polymerization of a caprolactan or amino acid (nylon 6). The thermal decomposition of nylons (melting point between 172° to 260° C) begins with a primary scission of the -NH-CH2- bond followed by a complex series of secondary reactions; at temperatures of 350° C, the initial

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[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

evolution of HCN, NH$_3$ (ammonia), and CO begins. At higher temperatures (600° C), nylon fibers melt and drip with the evolution of small NOx (nitrogen oxides) gas concentrations. Additives such as halogen compounds, antimony trioxide, phosphorus-nitrogen containing, and sulphur compounds are added to impart fire retardancy.

Wool is a natural polyamide regarded as a relatively nonflammable fiber although it can be ignited by a sufficient heat source. On combustion it yields HCN, CO, small quantities of NOx gas concentrations, and moderate amounts of smoke. However, wool, during its thermal degradation, does not melt or drip, so it is less dangerous than most synthetic polyamides; furthermore, the time to

death has been found to increase from 5.8 to 10.4 min, and the time to incapacitation from 4.5 to 7.3 min as wool content of the material decreased from 99 to 85 pct (16). Wool may be treated with flame retardants such as inorganic compounds (boric acid and borax), metal compounds (titanium, zirconium, and tin), and reactive organo-phosphorus compounds (phosphonium chloride or hydroxide).

Cotton batting is a natural cellulosic fiber treated with small amounts of halogenated flame retardants. The fiber has been found to yield large quantities of CO at high temperatures.

EXPERIMENTAL SYSTEM

The system (fig. 1) consists of an approximately 20-L furnace whose temperature rises automatically from ambient at a rate depending on the set temperature, which ranges from 100° to 1,200° C (fig. 2). A universal load cell, located under the furnace floor, contacts a sample-cup

pedestal, and transmits sample weight loss (voltages) via a bridge amplifier to a strip-chart recorder. A vacuum pump draws ambient air (10 L/min) continuously into the furnace, via an opening at the center of the furnace door, and pumps the resulting combustion air into the CO, CO$_2$,
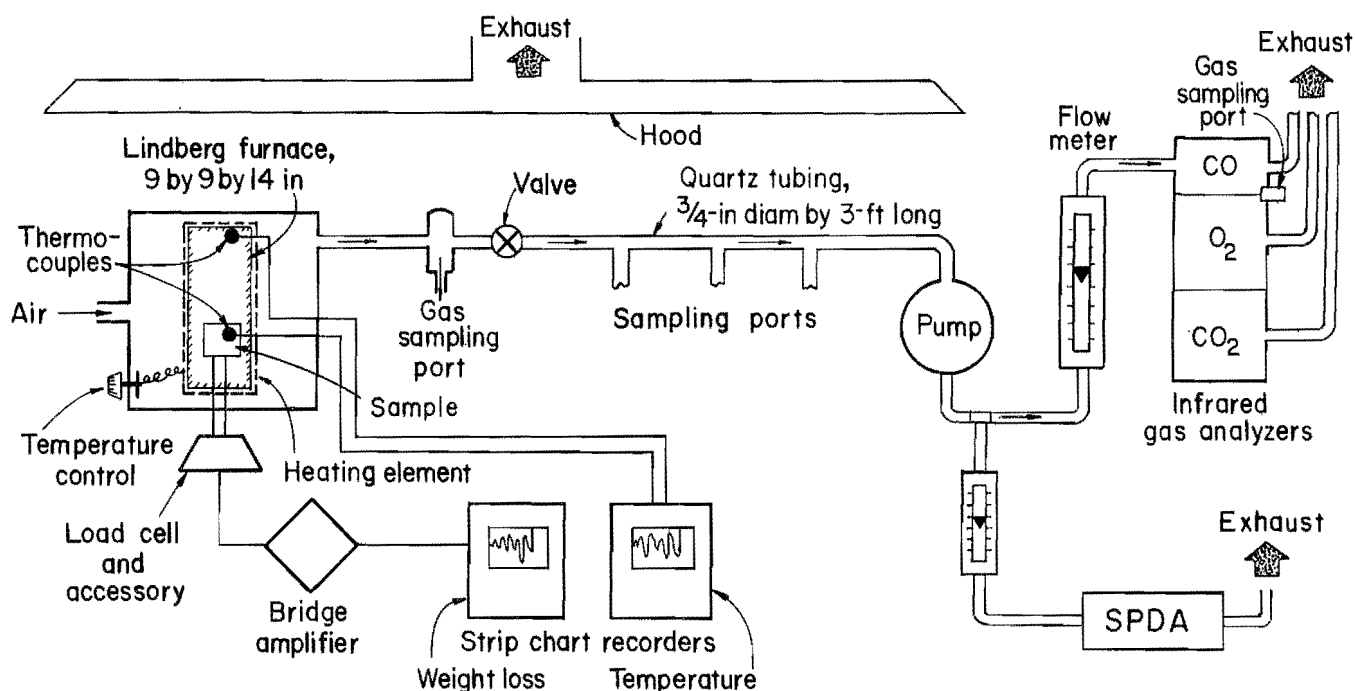
Figure 1.—Experimental system.

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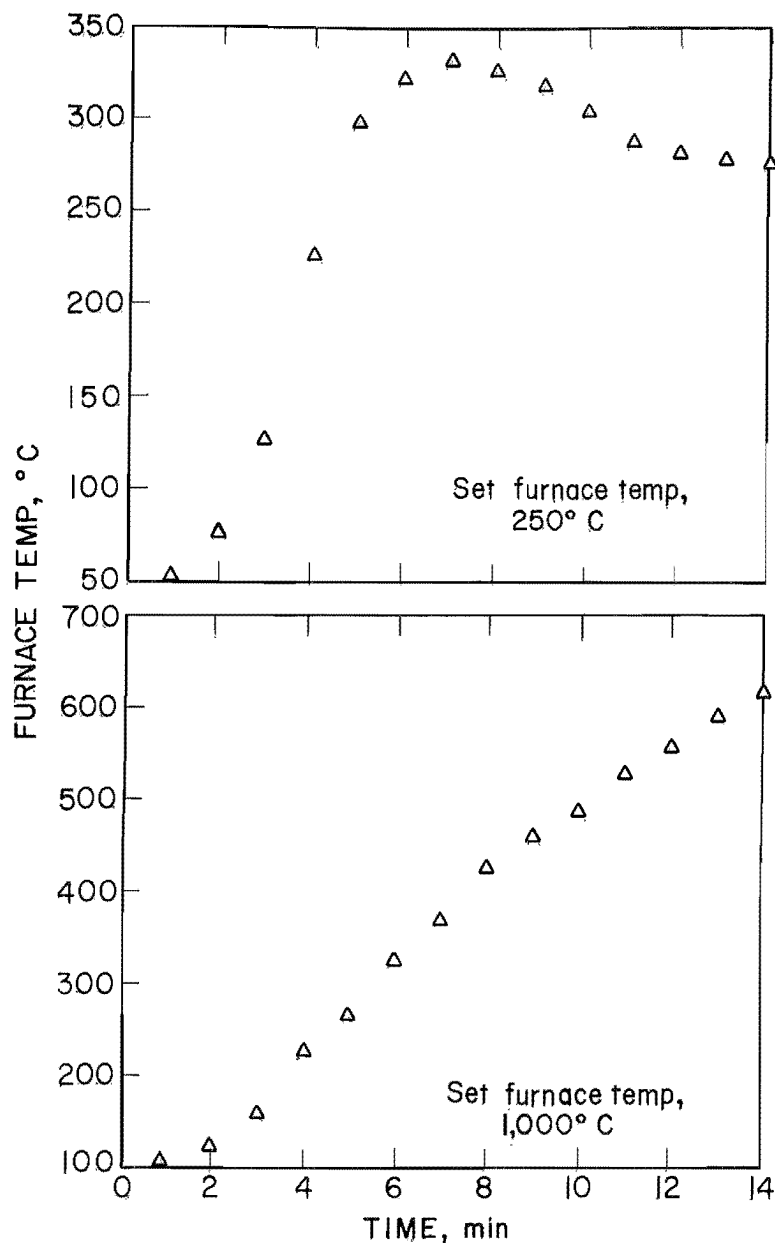
Figure 2.--Furnace temperature versus time at set furnace temperatures
of 250° and 1,000° C.

and O_2 gas analyzers and into the submicrometer particle detector analyzer (SPDA) (1.6 L/min) (17). Combustion air (10 L/min for a 14-min duration) also was directed into a filter cassette, which was connected to an impinger, and placed before the pump, to recover the HCN (gaseous and aerosol), and mass particulates. Flow meters installed between the pump outlet, the gas analyzers, and the SPDA

provide visual flow indication. The SPDA voltages are used to compute the d_g, the n_o, and the $d_g n_o$. A data acquisition system continuously acquires (10-s intervals), computes, and stores data of sample and furnace temperatures, airflows, sample weight loss, and the SPDA initial (without smoke) and experimental (with smoke) voltages.

EXPERIMENTAL PROCEDURE

Two sets of experiments (five experiments in each set; each experiment repeated three times) were performed at set furnace temperatures of 250° C (rising from ambient at ~30° C/min; reaching its maximum of ~300° C approximately at the 9th min), and 1,000° C (rising from ambient at ~40° C/min; reaching its maximum of ~600° C at the 14th min) (fig. 2) for a 14-min duration, with 1-g samples of treated and untreated flexible polyurethane foams, nylon and wool fabrics, and treated cotton batting. An additional set of experiments was performed at 1,000° C set furnace temperature to recover the gaseous and aerosol HCN, and mass particulates. A list of the materials is reported in table 1.

A 1-g sample was placed in a 2.5-cm-diam sample-cup, and the furnace was set at the desired temperature with a furnace airflow of 10 L/min, 1.6 L/min of which, as combustion air, was directed into the SPDA; the remainder of the combustion air was directed into the gas analyzers and into the exhaust hood. During the experiments at 250° C, HCN and CO concentrations were measured with detection tubes at 0.1-g sample weight loss. During

the experiments at 1,000° C to recover HCN, the combustion air (10 L/min for a 14-min duration) was directed into a filter cassette to determine the HCN aerosol embedded on particulates, and the mass of particulates. The cassette was connected to an impinger (containing 100 mL of analytical solution) to determine the HCN in the gaseous form. The filter was weighed, and together with the solution was analyzed by the Occupational Safety and Health Administration (OSHA) 7904 method for cyanide; the nitrogen content of the material was determined by the American Society Testing Material (ASTM) Kgeldahl method; the cyanate content of the material was determined by the modified method for cyanates in liquid; the chlorine content of the material was determined by the ASTM oxygen-bomb-combustion-selective-electrode method. Syringe grab samples, stored in sealed containers, were analyzed for CO, CO_2 and O_2 concentrations by gas chromatography. Other variables measured as a function of time were the sample mass weight loss, the furnace temperatures, and the SPDA voltages.

DATA REDUCTION AND ANALYSES

At 250° C set furnace temperature and 14-min duration, d_g (centimeter; reported as micrometer), n_o (particle per cubic centimeter), and $d_g n_o$ (particle per square centimeter) were calculated. Also, under the 250° C conditions, HCN (part per million), CO (part per million), CO_2 (part per million) and O_2 (percent) concentrations, the sample mass weight loss (gram), and the furnace temperature (°C) were measured. The HCN and CO

concentrations measured at 0.1-g mass weight loss, adjusted to 1-g weight loss, yielded the HCN and CO loads (part per million per gram). The CO loads, subsequently, reduced to HCN values by dividing each CO load by a factor of 40, because CO is 40 times less dangerous than HCN, were combined with the HCN loads yielding the CO-HCN loads (part per million per gram).

Table 1.—Description and nitrogen, cyanates, and chlorine contents, percent of materials investigated

Material	Description	Nitrogen	Cyanates	Chlorine
Flexible polyurethane foam:				
[1]Treated (Pr)	Based on toluene diisocyanate; treated with chlorine for fire retardancy.	4.79	0.025	4.97
Untreated (Pn)	. . do.	4.78	.025	0
Nylon fabric (Ny)	Based on polymerization of amino acid, untreated.	11.46	.09	0
Wool fabric (Wl)	Tinted wool fabric, untreated . . .	13.25	1.4	0
Cotton batting (Cr)	Natural fiber, treated	.24	.0004	.09

[1]With chlorine.

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At 1,000° C set furnace temperature, stage of combustion at which most of the HCN evolve, the gaseous HCN (microgram), the HCN aerosol (microgram), and the mass particulates (milligram) on which the HCN aerosol embed itself were measured. The HCN concentrations (microgram per gram), and the mass particulates (milligram per gram) have been treated as load values because they evolve during the complete decomposition of 1-g sample. The HCN gaseous load and the HCN aerosol load yielded the total HCN load (microgram per gram).

Also, under the 1,000° C conditions, d_g, n_o, and $d_g n_o$ have been measured. The $d_g n_o$ is obtained from the ratio of the SPDA experimental and initial current output (I_e/I_o) following the relationships in equation 1 (fig. 3).

$$I_e/I_o = 1/(K\ d_g n_o)(1\text{-exp}\ (\text{-}K\ d_g n_o)\ ), \qquad (1)$$

where $\quad$ K $\quad$ = charging constant (K = 0.012 cm^2/p).

Once the $d_g n_o$ is determined, d_g can be obtained from equation 2,

$$d_g = (\text{exp}\ ^{I_c/d_g n_o\text{-}1})/(I_c), \qquad (2)$$

I_c $\quad$ = SPDA charged particle current.

The sum of $d_g n_o$ values yielded the $d_g n_o$ loads (particle per square centimeter per gram).

CO, CO_2 and O_2 concentrations, sample mass weight loss, and furnace temperature also were measured.

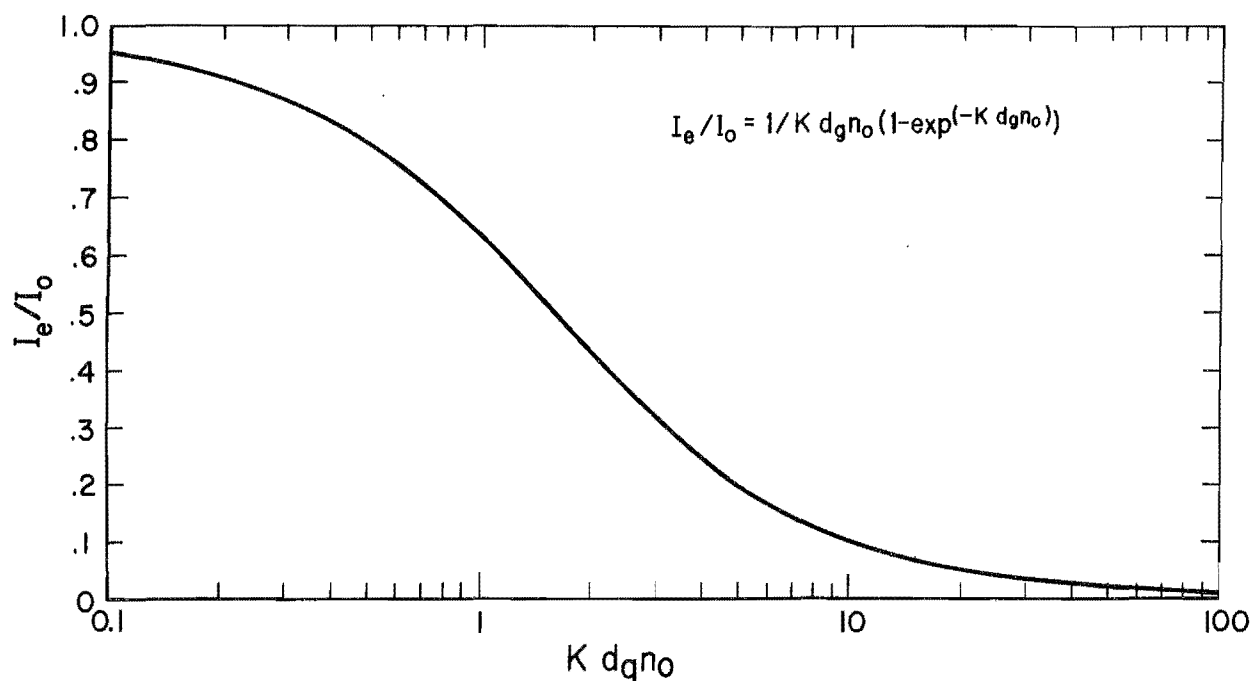$$I_e/I_o = 1/K\ d_g n_o\ (1\text{-exp}^{(\text{-}K\ d_g n_o)})$$

Figure 3.—SPDA current ratio (Ie/Io) as function of smoke particle diameter-concentration product ($d_g n_o$).

RESULTS AND DISCUSSION

At 250° C set furnace temperature, the wool sample, followed by the nylon and the polyurethane foam samples, released the highest HCN concentrations at 0.1-g sample mass weight loss, depending on the nitrogen and cyanate contents of the material, yielding the highest HCN loads (table 2), and the highest $d_g n_o$ values (fig. 4). The cotton batting released extremely insignificant HCN concentrations, yielding extremely small HCN loads, and small weight loss. The wool and the nylon samples had, also, extremely small weight loss, at the latest time (wool) (table 3). On the contrary, the foam samples had the largest weight loss, at the earliest time; conditions that allow the release of the HCN load earlier, at a faster rate, and therefore, increasing the hazard of these materials during fire. Furthermore, the foam samples underwent extensive physical changes (friable and viscous to the touch), yielding the largest amount of submicrometer smoke particles (table 4 and figs. 5-6). The nylon sample also underwent extensive physical change (melted substance), yielding, however, small amounts of particles of extremely small diameter. By contrast, the wool and the cotton samples underwent very little physical changes (browned), with the latter yielding extremely small amount of particles (table 4 and figs. 5-6).

Large CO concentrations were released by the foam samples (table 3 and fig. 7), yielding the highest CO loads (table 2), which reduced to HCN values increased significantly the CO-HCN loads, and therefore, the hazard of these materials during fire. On the contrary, the nylon sample, followed by the wool sample released the lowest CO concentrations, yielding the lowest CO loads.

At 1,000° C set furnace temperature, all samples underwent complete decomposition; however, the foam and nylon samples decomposed much earlier, at faster rates (table 3) (dripping flaming droplets). Under these conditions, the wool sample, followed by the nylon and by the foam samples released the highest HCN concentrations (mostly in the gaseous form), depending on the nitrogen and cyanate contents of the material, yielding the highest HCN, $d_g n_o$, and mass particulate loads (table 2). Large CO concentrations were released by the foam and cotton samples (table 3 and fig. 7); on the contrary, the lowest CO concentrations were released by the nylon and wool samples. The highest mass particulates on filter (table 2) were released by the wool and by the foam samples.

Table 2.—Toxic load data; furnace airflow 10 L/min

Material investigated[1]	250° C				1,000° C			
	HCN, ppm/g	CO, ppm/g	[2]HCN, ppm/g	[3]CO-HCN, ppm/g	[4]HCN, μg/g		Mass particulate, mg/g	$d_g n_o$, p/(cm² · g)
					Gaseous	Total		
Pr	14	1,100	27.5	41.5	425	430	5.3	800
Pn	14	1,000	25	39	420	425	5	785
Ny	38	300	7.5	45.5	1,125	1,132	1.6	1,000
Wl	62	600	15	77	1,850	1,868	6.9	1,400
Cr	2	1,100	17.5	30	30	32	3	637

[1]1-g sample. See table 1 for description.

[2]Carbon monoxide load values normalized to hydrogen cyanide values. The carbon monoxide values have been scaled down by a factor of 40 because carbon monoxide is at least 40 times less toxic than hydrogen cyanide.

[3]CO (as HCN) and HCN load values.

[4]Hydrogen cyanide total is the sum of the hydrogen cyanide in the gaseous and aerosol forms.

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Table 3.—Oxidative thermal degradation data; furnace airflow 10 L/min

Material investigated[1]	Time, min	250° C					1,000° C				
		CO, ppm	CO₂, ppm	O₂, pct	WL, g	F. Temp, °C	CO, ppm	CO₂ ppm	O₂, pct	WL, g	F. Temp, °C
Pr	6	15	500	20.9		239	33	700	20.8		226
	8	70	920	20.8		306	245	1,500	20.7		326
	9	124	950	20.8	0.50	306	1,400	1,900	20.5	0.98	364
	10	318	1,060	20.7		302	2,670	23,400	17.5		409
	12	457	1,130	20.7		291	855	4,500	20.2		481
	14	440	1,070	20.7		277	642	3,100	20.4		542
Pn	6	30	490	20.8		257	37	600	20.8		254
	8	95	930	20.8		306	427	1,600	20.6		349
	9	112	900	20.8	.40	302	2,460	23,000	17.7	.98	388
	10	166	880	20.8		297	1,180	16,700	18.8		442
	12	184	810	20.8		285	615	4,700	20.2		505
	14	130	700	20.8		271	476	3,100	20.4		566
Ny	6	33	480	20.8		257	36	520	20.8		225
	8	29	490	20.8		305	31	550	20.8		325
	9	20	490	20.8	.18	304	51	620	20.8	.99	360
	10	17	480	20.8		299	189	920	20.8		410
	12	13	490	20.8		285	785	25,400	17.4		480
	14	10	450	20.8		272	517	5,370	20.4		540
Wl	6	21	500	20.9		233	25	490	20.8		267
	8	58	690	20.8		303	130	880	20.8		345
	9	47	740	20.8	.15	304	400	1,440	20.7	.97	388
	10	34	720	20.8		299	1,320	2,100	20.5		428
	12	21	680	20.9		286	731	3,270	20.4		506
	14	13	630	20.9		278	310	2,480	20.5		570
Cr	6	72	560	20.8		257	25	480	20.82		243
	8	115	640	20.8		307	1,200	2,260	20.61		335
	9	92	660	20.8	.25	304	3,020	5,300	20.13	.86	378
	10	45	1,190	20.8		299	2,200	4,580	20.29		415
	12	49	630	20.9		285	1,170	4,620	20.30		485
	14	33	580	20.8		272	641	3,670	20.37		544

WL   Weight loss.
F. Temp.   Furnace temperature.
[1]1-g sample. See table 1 for description.

Table 4.—Smoke particle characteristic data; furnace airflow 10 L/min

| Material investigated[1]	Time, min	250° C			1,000° C		
		d_g, μm	n_o, 10^3 p/cm^3	$d_g n_o$, p/cm^2	d_g, μm	n_o, 10^3 p/cm^3	$d_g n_o$, p/cm^2
Pr	6	0.13	25,000	152	1.0	695	50
	8	.084	837	318	.033	81,000	125
	9	.015	216,000	306	.009	127,000	73
	10	.055	108,000	222	.086	993	26
	12	.087	23,500	185	.2	7,320	92
	14	.075	27,100	202	.36	10,050	100
Pn	6	6.0	329	46	1.9	257	35
	8	.02	199,000	324	1.5	51,320	70
	9	.06	42,800	200	.005	87,000	400
	10	.07	33,000	188	1.4	1,760	18
	12	.4	3,150	108	.4	181	3
	14	2.0	368	49	.7	1,260	79
Ny	6	.002	31.2	19	1.9	101	16
	8	.004	3.3	10	3.0	89.5	23
	9	.09	3	5	.8	590	34
	10	.007	3.9	2	.25	22,200	162
	12	.001	13.5	5	.4	176,000	267
	14	.24	.3	2	.7	265	6
WI	6	.4	3.8	24	10.0	14.3	20
	8	.02	233,000	326	.44	7,880	182
	9	.007	431,000	368	.044	68,800	250
	10	.01	345,000	374	.024	138,000	303
	12	.04	48,000	189	.6	1,540	52
	14	.3	3,070	75	.22	6,440	128
Cr	6	5.0	2,820	91	.1	1,440	76
	8	.3	4,190	118	.5	4,060	86
	9	.6	1,820	89	.14	6,780	87
	10	2.0	364	58	.24	6,680	102
	12	11.0	58.6	16	.5	911	49
	14	1.1		4	.6	105	43

[1]1-g sample. See table 1 for description.
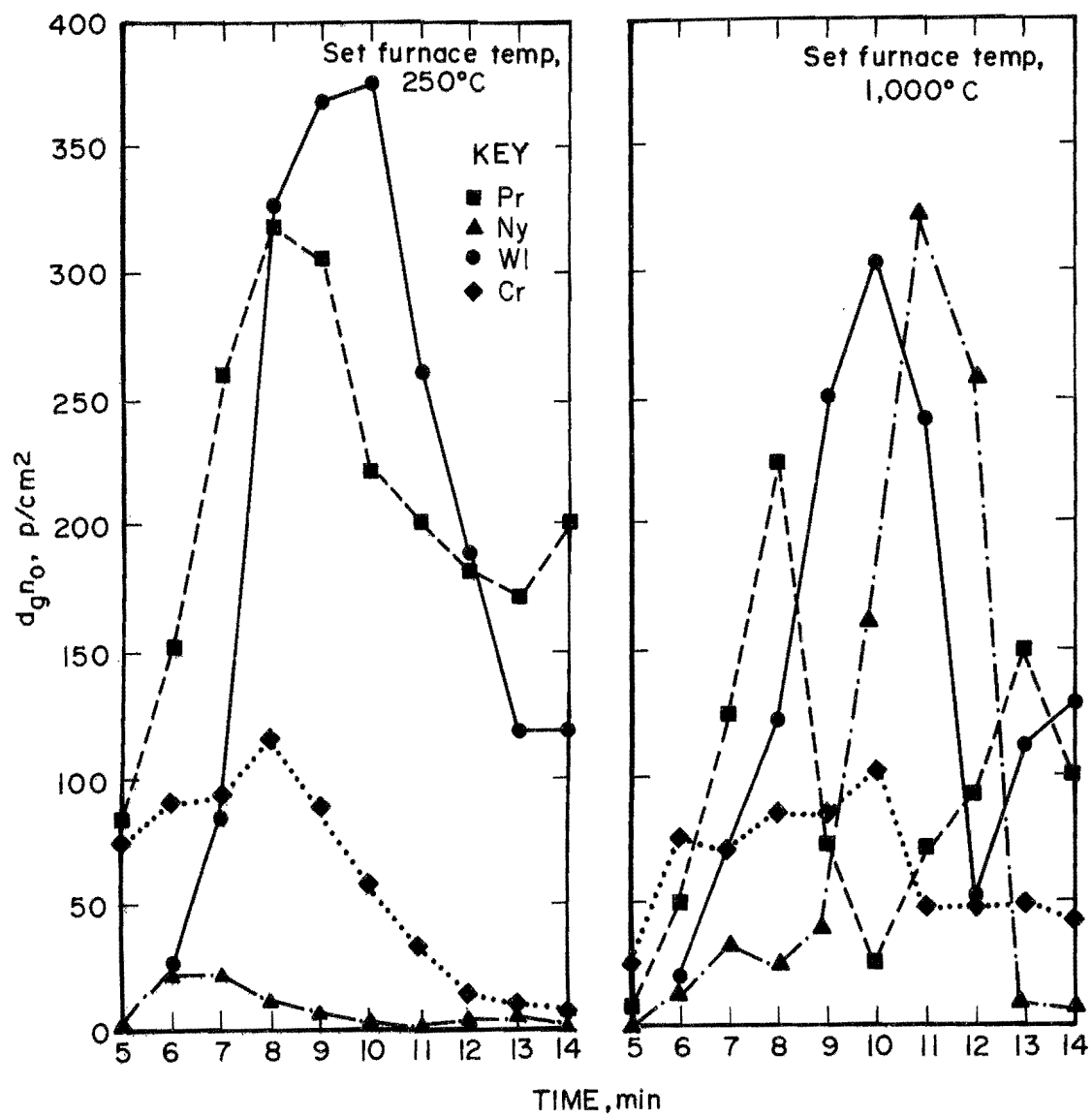
Figure 4.—Smoke particle diameter-concentration product ($d_g n_o$) versus time at 250° and 1,000° C.
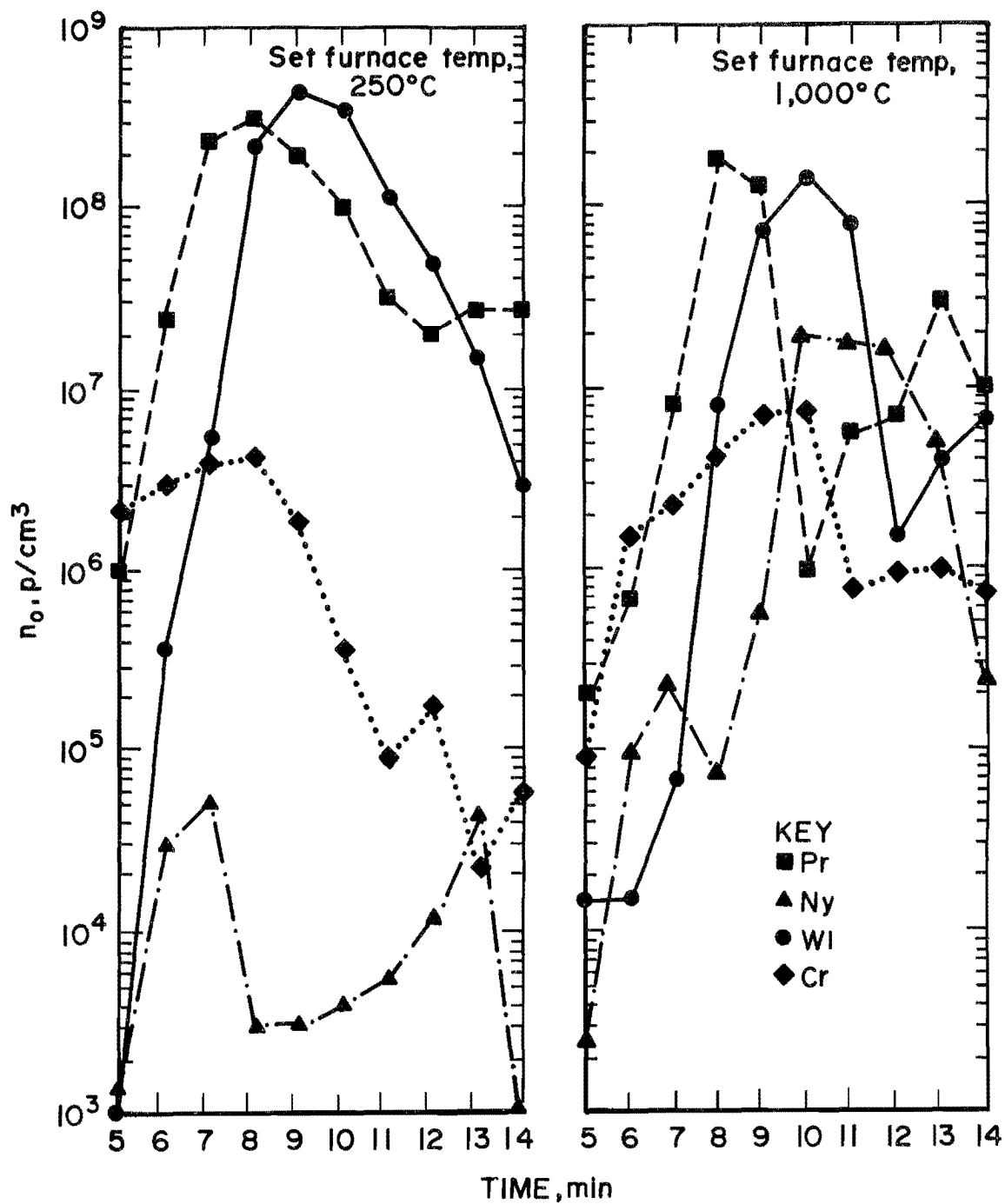
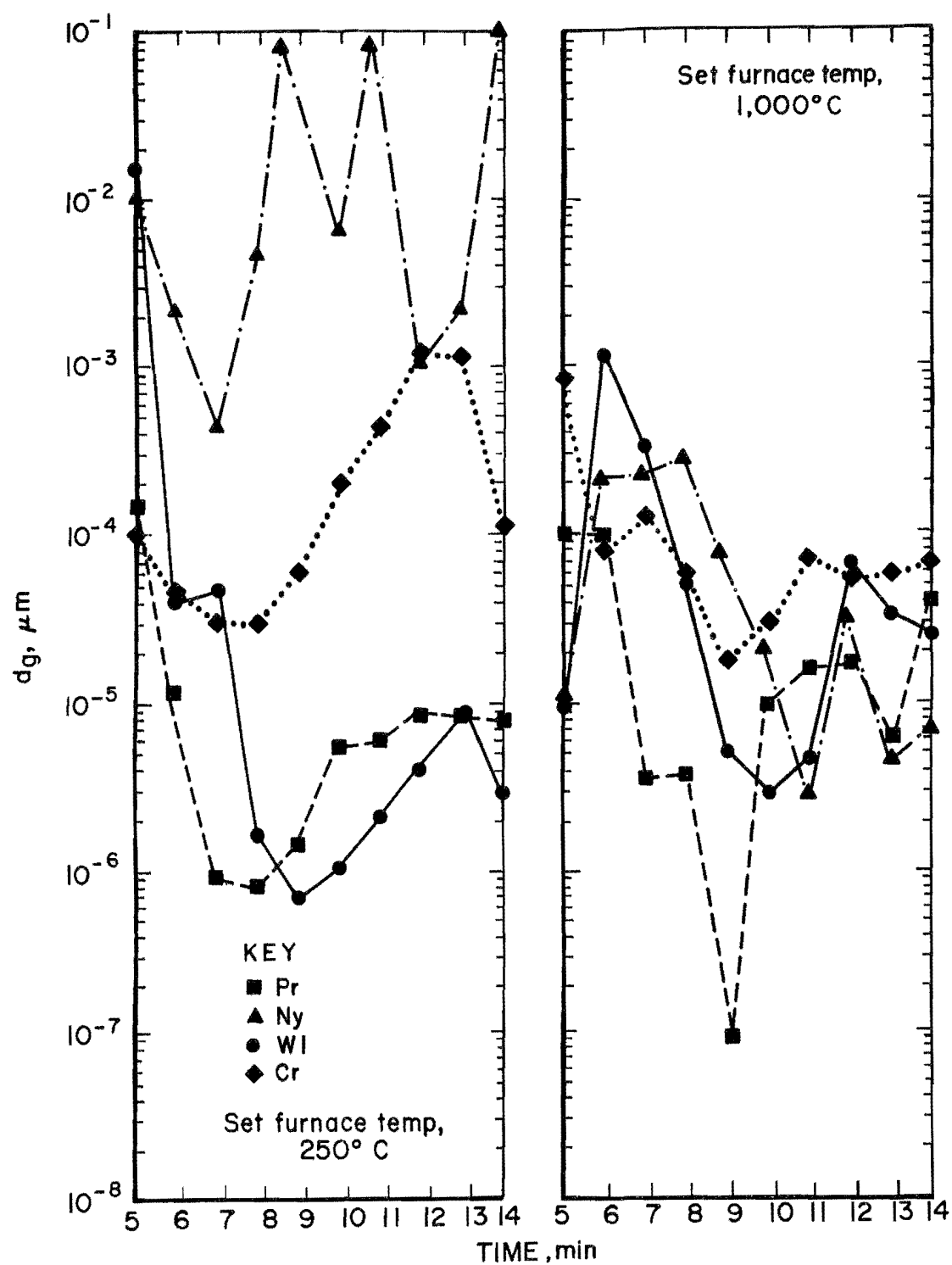Figure 5.—Smoke particle concentration (n₀) versus time at 250° and 1,000° C.

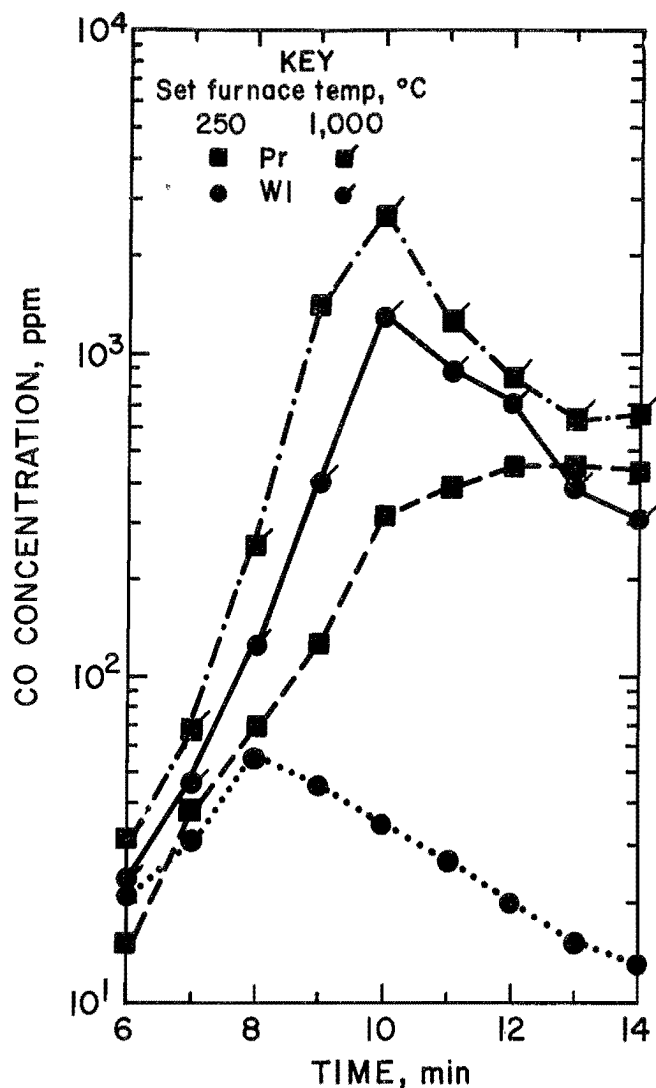Figure 6.—Smoke particles average diameter (d_g) versus time at 250° and 1,000° C.

Figure 7.—CO concentration versus time at 250° and 1,000° C.

Correlations ($r = 0.80$) (figs. 8-11) were calculated at 250° C set furnace temperature between the $d_g n_o$ load and the toxic loads (HCN load and CO-HCN loads); between the $d_g n_o$ load and the HCN loads (gaseous and total) at 1,000° C set furnace temperature; between the total HCN load and the nitrogen content of the material; and between the total HCN load and the cyanate content of the material.
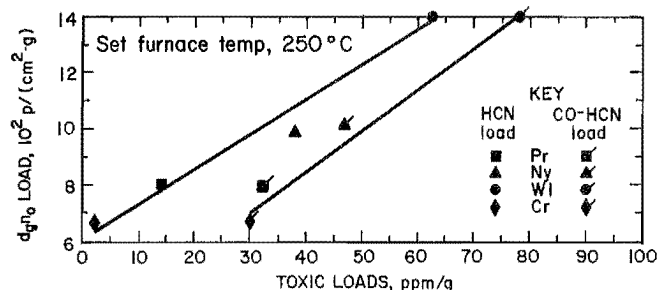

Figure 8.—Smoke particle diameter-concentration product load ($d_g n_o$ load) versus toxic loads (HCN load, and CO-HCN load) at 250° C.
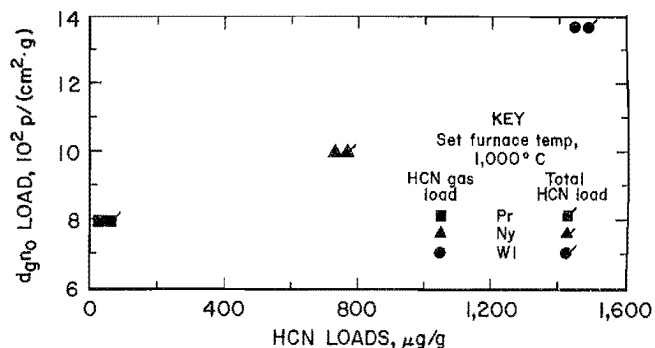

Figure 9.—Smoke particle diameter-concentration product load ($d_g n_o$ load) versus HCN loads (gaseous and total) at 1,000° C.
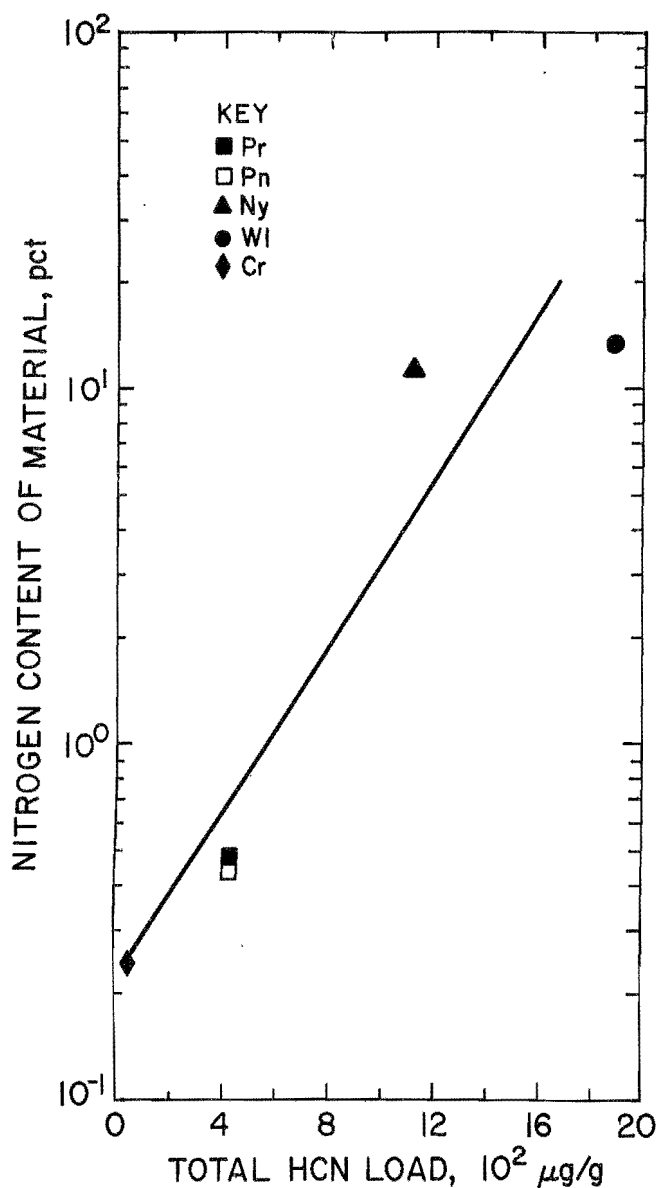
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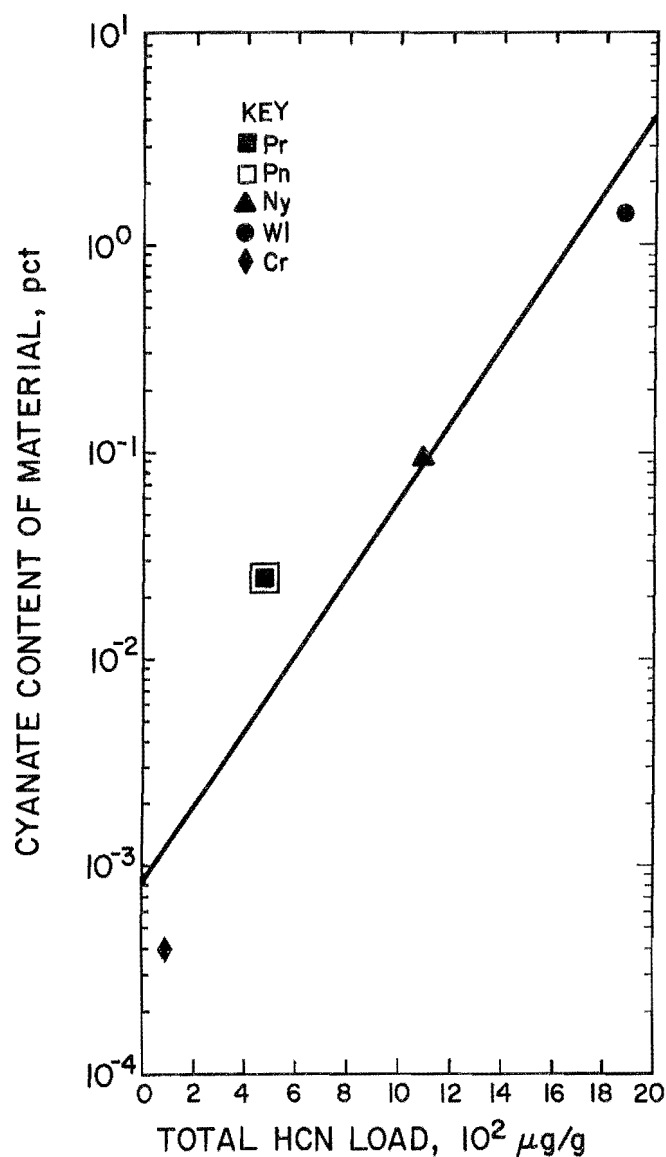Figure 10.—Total HCN load versus nitrogen content of material.

Figure 11.—Total HCN load versus cyanate content of material.

CONCLUSIONS

According to these findings, the product of the smoke particle diameter-concentration, $d_g n_o$, correlates directly with the hydrogen cyanide concentrations (gaseous and aerosol); the concentrations being mostly in the gaseous phase. The higher the concentrations, depending on the nitrogen and cyanate content of the material, the higher the $d_g n_o$ values. The wool sample, followed by the nylon fabric and the polyurethane foam samples, released the highest hydrogen cyanide concentrations, yielding the highest HCN loads, due to the large nitrogen and cyanate contents of the materials, and the highest $d_g n_o$ values. As expected, the lowest hydrogen cyanide concentrations were released by the cotton batting. These samples also yielded the largest mass particulates, and particles of submicrometer diameter. However, of extreme importance, is the fact that the polyurethane foam samples had extremely large weight loss, even at lower temperature (~300° C), at an earlier time and at faster rates; conditions that allow

the release of the hydrogen cyanide load earlier and faster. Furthermore, only the foam sample underwent extensive physical changes (melted and dripping substances) even during the early stage of combustion (~300° C); the cotton and wool samples remained physically unchanged, even during the later (>400° C) stage of combustion. As expected, the lowest hydrogen cyanide concentrations were released by the cotton sample, due to the extremely low nitrogen and cyanate contents of the material.

Large CO concentrations were released by the foam and cotton samples; the foam sample released large CO concentrations, even at lower temperatures. CO concentrations, reduced to HCN values, increased significantly the toxicities of the foam materials. The lowest CO concentrations were released by the nylon and wool samples, even at higher temperatures.

In conclusion, the HCN load, depending on the nitrogen and cyanate contents of the material, CO loads, and material's ease of thermal decomposition determine the time at which dangerous conditions are reached; a shorter time implies a more dangerous material.

The excellent correlation of the smoke particle characteristic $d_g n_o$ with the HCN and CO concentrations suggests its development and use as a test parameter, for the development of a simpler and less expensive method of assessing the toxic hazard of these materials under fire conditions.

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